Two decades of trace metals monitoring in the Spanish Mediterranean Sea with wild mussels: geographical features and temporal trends

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ABSTRACT

Since 1991, the Instituto Español de Oceanografía has monitored the concentrations of trace metals in wild mussels from the Mediterranean coast of Spain to define geographical distributions and temporal trends. While Cu concentrations presented fairly uniform geographical distributions, Zn concentrations were higher in the southern coast, probably influenced by the inflow of Atlantic Sea waters from the Gulf of Cadiz that are enriched in this element due to the outflows of Guandiana, Tinto and Odiel rivers. Opposite, As concentrations are higher in the northern sites, associated with the geology of the surrounding area of the Pyrenees where an important minery activity exists. Regarding Cd, Pb and Hg, levels are quite homogeneous along the coast with some hotspots as Portman Bay in the case of Cd and Pb or the area around Barcelona when talking about Pb and Hg. An improvement in environmental conditions along the Mediterranean coasts of Spain is evident having a look at trace metal temporal trends, despite that some metal levels resulted above the Background Assessment Concentrations given by OSPAR to assess potentially harmful occurrences.

INTRODUCTION

In 1991, the Instituto Español de Oceanografía started a "Wild Mussel" Marine Pollution Monitoring Program using mussels from the Mediterranean coastal area. This Program evolved as a response to the Program for the Assessment and Control of Pollution (MEDPOL, Barcelona Convention), in the Mediterranean region. Based on the "Mussel Watch" concept, the Program has the main purpose of monitoring selected chemical pollutants in Spain's coastal zones to identify geographical distributions and temporal changes. This information is also used to evaluate the environmental protection activities enforced in Spain within the European Union Marine Strategy Framework Directive which requires that EU Member States take action to achieve or maintain a Good Environmental Status (GES) in their coastal marine regions by the year 2020.

Following the concept of the "Mussel Watch", bivalve molluscs, specially the Mytilus species, are particularly suited for monitoring purposes and their use has been recommended by international organizations/conventions. Mussels can accumulate metals to concentrations several orders of magnitude higher than levels in the surrounding aquatic media making them excellent tracers to monitor coastal water quality.

Metals occur naturally in the environment; however, anthropogenic sources (e.g., industrial, domestic, and agricultural activities) are responsible for most of the elevated concentrations observed in coastal waters. This study presents an assessment of the geographical distribution and temporal trends of target trace metals after two decades of monitoring wild mussels (M. galloprovincialis) from the Mediterranean Spanish coast.

MATERIAL AND METHODS

Wild mussel (*M. galloprovincialis*) samples were collected in 21 locations along the Mediterranean littoral of the Spanish Coast from Cadaques to the Strait of Gibraltar. These sites were selected taking into consideration bivalve availability, accessibility to the sites, and representativeness of surrounding areas, but outside the zone of initial dilution of contaminants. Reference sites and hot spot areas are included among these stations. All locations were sampled on a yearly basis. At each station, 3 pools of 80 mussels with lengths between 3 and 4 cm were sampled. Mussel collection was performed manually, at low tide, during the same time of the year (May to June) to minimize variations caused by differences in the mussels' physiology and minimize the effect of seasonal environmental changes [1,2]. Following collection, mussels were placed in water from the same location to eliminate pseudofeces. After 24 h, the soft tissues were separated from the shells, triturated with an Ultraturrax and an aliquot of the homogenized sample was withdrawn to determine its dry weight. The remaining tissue was freeze-dried, homogenized with a mixer mill, and stored in acid washed glass vials until analysis.

Analytical procedures were kept similar during the two decades study. Tissue samples were processed with nitric acid in Teflon digestion bombs placed in conventional or microwave ovens. Briefly, 0.3-1 g of freeze–dried mussel sample was placed in a Teflon reactor and, after the addition of 1 ml of Milli-Q water and 6 ml of concentrated Merck Suprapur nitric acid, the reactor was heated with an appropriate temperature ramp. Target metals, with the exception of Hg, were analyzed either by flame AAS (F-AAS, AAnalyst 100) for As, Cu and Zn, while Cd and Pb were determined by graphite furnace with Zeeman background correction (ZGF-AAS, 4110 ZL, Perkin-Elmer). Total Hg was determined by cold vapor technique, employing a Perkin-Elmer FIMS-400 system ($SnCl_2$ as reducing agent). Detection limits were 0.003, 0.005, 0.050, 0.50, 0.30, and 0.30 mg/kg dry weight (mg/kg dw) for Hg, Cd, Pb, Cu, Zn, and As, respectively.

The analytical methods were validated and include rigorous Quality Assurance/Quality Control (QA/QC) samples (i.e., procedural blanks, duplicated samples, and certified reference materials) to ensure that the data produced was accurate and reproducible.

RESULTS AND DISCUSSION

Metal median, mean concentrations and ranges are shown in Table 1. With the exception of some high values of As, Cd or Pb, associated to hotspot sites, levels are similar to the ones reported by [3] and similar monitoring studies referred therein.

Table 1. Summary of the concentrations of trace metals (mg/kg dry weight) in wild mussels Calculated considering all sampling sites and years for each trace metal (Std = standard deviation).

Metal	Median	Mean ± Std	Range
Hg	0.143	0.174 ± 0.110	0.025-0.739
Cd	0.620	0.699 ± 0.391	0.209-3.05
Pb	2.49	5.57 ± 19.6	0.648-271
Cu	6.28	6.34 ± 1.66	2.32-13.1
Zn	152	189 ± 101	48.9-584
As	16.9	20.0 ± 11.6	8.60-86.0

Geographical distribution. After the calculation of the mean concentrations of each metal for each sampling site, different geographical trends can be observed depending on the metal considered. Regarding Hg, values are quite homogeneous among stations, oscillating between 0.10-0.20 mg/kg dw. Higher values were found in the area between Barcelona and Peñíscola with the highest value found in the Delta del Ebro (0.35 mg/kg dw). Copper is the element that shows the most similar concentrations along the entire coast with values ranging 5.0-7.5 mg/kg dw with the exception of Barcelona (10 mg/kg dw). Cadmium concentrations varied between 0.4 and 0.8 mg/kg dw with the exception of three sites: Calahonda (1.1 mg/kg dw), La Herradura (1.1 mg/kg dw) and Portman (2.2 mg/kg dw). The historical mining activities and the remaining tailings in Portman Bay should be the reason of these enhanced levels of Cd in mussels. In this way, the highest Pb values were also found in this area (92.4 mg/kg dw) while the rest of the sites showed Pb levels ranging from 2.0 to 4.0 mg/kg dw with the exception of Barcelona (11.2 mg/kg dw) and Málaga (4.3 mg/kg dw). With respect to As and Zn, these metals showed opposite trends as Zn values increased towards the Strait of Gibraltar (from 100 to 350 mg/kg dw) (Fig. 1) while As levels decreased (from 40 to 15 mg/kd dw). The high As levels found in Cadaqués, Islas Medas and Blanes are associated to the Arseno-pyritic formation of the Pyrinees.

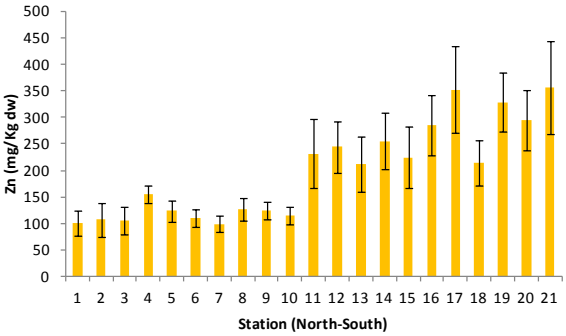

Fig. 1. Average Hg, Cd and Pb concentrations in mussel tissues from the N-NWSpanish coasts collected in 2000, 2005 and 2010. Error bars are the standard deviation (95th confidence interval).

Temporal trends. Generally, metal concentrations in mussels decreased from the nineties to the present days. However, some exceptions were observed. Copper levels showed a net increase in Cadaqués and Valencia, Zn values increased also in Cadaqués and Torrox and As concentrations increased in Málaga and the Strait of Gibraltar. The case of Cadmium is quite surprising as levels increased in all the stations north of Tarragona and south of Almuñecar a decreasing trend was observed in all the stations between Ebro and Calahonda.

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